Supporting Information

Iron Porphyrin-Based Conjugated Network Wrapped around Carbon Nanotubes as a Noble-Metal-Free Electrocatalyst for Efficient Oxygen Reduction Reaction

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Experimental details

Materials

All reagents, including triisopropylsilylacetylene (97.0%), n-butyllithium (2.5 M solution in n-hexane), pyrrole (99.5%), boron trifluoride diethyl etherate (BF$_3$·Et$_2$O, 98.0%), ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O, 98.0%), tetrabutylammonium fluoride (1.0 M solution in tetrahydrofuran), copper(I) chloride (CuCl, 99.0%), carbon nanotubes (CNTs, OD:1~2 nm, 90%), 5 wt% Nafion solution, dipotassium hydrogen phosphate trihydrate (K$_2$HPO$_4$·3H$_2$O, 99%), potassium dihydrogen phosphate (KH$_2$PO$_4$, 99.5%), boric acid (H$_3$BO$_3$, 99.9%), nitric acid (HNO$_3$, 65.0%~68.0%), and hydrochloric acid (HCl, 36.0%~38.0%) were purchased from Aldrich or Acros and used as received unless otherwise noted. All organic solvents, such as tetrahydrofuran (THF, 99%), diethyl ether (Et$_2$O, 99.7%), methanol (MeOH, 99.5%), ethanol (EtOH, 99.7%), petroleum ether (60~90°C), dichloromethane (CH$_2$Cl$_2$, 99.5%), chloroform (CHCl$_3$, 99%), dimethylformamide (DMF, 99.5%), tetramethylethylenediamine (TMEDA, 98%), and N-methylpyrrolidone (NMP, 99%) were purchased from China Medicine Shanghai Chemical Reagent Co. All aqueous electrolyte solutions were freshly prepared with Millipore water (~18.3 MΩ·cm resistivity at room temperature).

Synthesis

Purification of CNTs. CNTs were purified by oxidative treatment with HNO$_3$ and the details are provided as follows: CNTs (80 mg) were immersed in 200 mL concentrated HNO$_3$ (~35 %) and gently sonicated in a sonic bath (150 W max) for 30 min. Then, the suspension was stirred at 100°C for 12 hours. After cooling to room temperature, the
resulting CNTs were collected and thoroughly washed with 2.0 M NaOH (20 mL×2), deionized water (20 mL×3), 1.0 M HCl (20 mL×2), and deionized water (20 mL×5) sequentially until the filtrate was neutral. The purified CNTs were dried overnight in vacuum oven at room temperature.

3-(triisopropylsilyl)propionaldehyde and 5,10,15,20-tetrakis-(triisopropylsilylethynyl)porphyrin (1) were synthesized following the procedure reported in literature.\textsuperscript{[1, 2]}

5,10,15,20-tetrakis-(triisopropylsilylethynyl)porphyrin iron chloride (FeP-TIPS, 2). Porphyrin 1 (120 mg, 0.12 mmol) and FeCl\textsubscript{2}·4H\textsubscript{2}O (231 mg, 1.16 mmol) were dissolved in 30 mL DMF and refluxed overnight under argon atmosphere with stirring. After cooling to room temperature, CHCl\textsubscript{3} (20 mL) and 1.0 M HCl (50 mL) were added, followed by stirring for 1 hour. Then, CHCl\textsubscript{3} layer was separated, evaporated by rotavap, and dried under vacuum to yield a dark yellow solid (125 mg, ~96% yield).

UV-vis (CH\textsubscript{2}Cl\textsubscript{2}) \(\lambda_{\text{max}}\) (nm) 465, 565, 594. MALDI-TOF-MS \textit{m/z} = 1084.5591 [M-Cl]\textsuperscript{+}, Calcd. for \([\text{C}_{64}\text{H}_{92}\text{FeN}_{4}\text{Si}_{4}]^{+}\): 1084.5748 (Figure S1). Anal. Calcd for \([\text{C}_{64}\text{H}_{92}\text{ClFeN}_{4}\text{Si}_{4}]^{+}\): C, 68.57; H, 8.27; N, 5.00. Found: C, 68.24; H, 8.11; N, 4.85.

5,10,15,20-tetraethynyl-porphyrin iron chloride (FeP, 3). Porphyrin FeP-TIPS (100 mg, 0.09 mmol) was dissolved in anhydrous THF (20 mL) under argon atmosphere. Then, 360 \(\mu\text{L}\) of tetrabutylammonium fluoride (TBAF, 1.0 M in THF) was added. The mixture was stirred under ice bath for 3 hours. Thereafter, 20 mL of deionized water was added to generate precipitates. After filtration, the residue was thoroughly washed with deionized water (20 mL×3), MeOH (20 mL×3), and petroleum ether (20 mL×3)
to yield a green solid, which was dried under vacuum at room temperature (30 mg, ~68% yield). UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (nm) 457, 569, 607. MALDI-TOF MS $m/z = 460.0800$ [M-Cl]$^+$, Calcd. for [C$_{28}$H$_{12}$FeN$_4$]$^+$: 460.0411 (Figure S2). Anal. Calcd for C$_{28}$H$_{12}$ClFeN$_4$: C, 65.46; H, 2.75; N, 10.91. Found: C, 65.70; H, 2.66; N, 10.69.

**Synthesis of (FeP)$_n$-CNTs.** FeP (15 mg, 0.03 mmol) and CNTs (10 mg) were dispersed in NMP (150 mL) under sonication. After aging for one hour at room temperature, a freshly prepared suspension of 25 mg copper (I) chloride (0.25 mmol) and 100 μL TMEDA in 2 mL NMP was added. Then, the mixture was stirred for 48 hours under gentle O$_2$ steam at room temperature. The suspension was then filtered and the solid was washed thoroughly with NMP (20 mL×3), deionized water (20 mL×3), aqueous ammonia (5%, 20 mL×3), deionized water (20 mL), NMP (20 mL), deionized water (20 mL), THF (20 mL), and CH$_2$Cl$_2$ (20 mL) sequentially. The resultant (FeP)$_n$-CNTs was dried overnight under vacuum at room temperature.

**Preparation of FeP-TIPS mixed with CNTs (FeP-TIPS/CNTs).** FeP-TIPS (15 mg, 0.01 mmol) and CNTs (10 mg) were added into THF (15 mL). The mixture was sonicated for 30 min. Thereafter, the solvent was evaporated under rotavap and dried overnight under vacuum at room temperature.

**Characterization**

High-resolution mass spectrometry (HRMS) data were collected via a Bruker Daltonics Inc. LTQ Orbitrap XL hybrid Fourier Transform High-resolution Mass Spectrometer. UV-vis spectra were obtained on a UNIC-3802 spectrophotometer. The morphologies of the materials were examined by scanning electron microscopy (SEM, SIRION200
Schottky field emission scanning electron microscope with an acceleration voltage of 5 kV or 10 kV) and high-resolution transmission electron microscopy (HRTEM, JEM-2010 electron microscope operating at an acceleration voltage of 200 kV). Raman spectra were recorded on LabRamHR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo ESCALAB 250 X-ray photoelectron spectroscopy instrument with a 150-watt Al Kα excitation source at 1486.6 eV. XPS spectra were referenced to C 1s peak (285.0 eV).

**Electrochemical experiments**

All electrochemical tests were carried out with an electrochemical potentiostat (CHI760E, purchased from Shanghai Chenhua Instrument Co., Ltd.). The typical procedure for catalyst ink preparation is as follows: catalyst (2 mg, (FeP)_n-CNTs, CNTs, FeP-TIPS, FeP-TIPS/CNTs) was dispersed in 360 µL of ethanol and 40 µL of 5 wt% Nafion solution. The mixture was sonicated for 1 hour to form a black ink for electrocatalysis. Before each test, the glassy carbon (GC) rotating disk electrode (RDE, d =5 mm, 0.196 cm²) was polished to be mirror-like surface by alumina and rinsed with deionized water. 20 µL of (FeP)_n-CNTs, CNTs, and FeP-TIPS ink or 30 µL of CoP-TIPS/MWCNTs ink were carefully modified onto clean RDE and dried at room temperature. Electrochemical experiments were performed in a standard three-electrode system, consisted of a working electrode, an Ag/AgCl (3 M KCl) reference electrode, and a platinum wire as the counter electrode. The potentials in this paper are all versus reversible hydrogen electrode (RHE), according to the formula:

\[ E = E_{\text{appl}} + E_{\text{Ag/AgCl}} + 0.059 \text{ pH} \]
Where $E_{appl}$ corresponds to the applied potential vs. Ag/AgCl, $E_{Ag/AgCl}$ was tested before each measurement. The electrolyte was bubbled with O$_2$ for 20 min before each test, and O$_2$ purging was lasted when performing electrochemical measurements.

From Koutecky-Levich plots (K-L plots), the electron transfer numbers ($n$) involved in ORR were calculated according to the Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{J_L} = \frac{1}{B\omega} + \frac{1}{J_k}$$

Where $J, J_k$, and $J_L$ are the measured, kinetic, and diffusion-limiting current densities, respectively. $\omega$ represents the angular rotation speed, $B = 0.62nFC_O2D^{2/3}vr^{-1/6}$, $n$ is transferred electron number, $F$ is Faraday constant (96485 C/mol), $C_O2$ is the saturation concentration of O$_2$, $D$ is the diffusion coefficient of O$_2$, and $r$ is the kinematic viscosity of the electrolyte. In 0.1 M KOH solution, $C_O2$ is 1.2×10$^{-6}$ mol·cm$^{-3}$, $D$ is 1.9×10$^{-5}$ cm$^2$·s$^{-1}$, and $v$ is 0.01 cm$^2$·s$^{-1}$. The constant of 0.62 is applied when the rotating speed is expressed in rad/s.

The percentage of produced H$_2$O$_2$ and the electron transfer number ($n$) were calculated from the rotating ring-disk electrode (RRDE, 5.61 mm, 0.247 cm$^2$) data following the formula:

$$H_2O_2\% = \frac{2 \times I_r}{(N \times I_d)} \times 100$$

$$n = 4 \times \frac{I_d}{(I_d + I_r / N)}$$

Where $I_r$ is the ring current, $I_d$ is the disk current, and $N$ is the collection efficiency ($N$ is 0.37 in current work).
References.


Figure S1. High resolution mass spectrometry (HRMS) for FeP-TIPS (2).

Figure S2. HRMS data for FeP (3).
Figure S3. XPS Cl 2p spectrum of (FeP)$_n$-CNTs
Figure S4. The survey scan of XPS for FeP-TIPS/CNTs.
Figure S5. CVs of (FeP)$_n$-CNTs in Ar-saturated 0.1 M KOH (black plot) and in O$_2$-saturated 0.1 M KOH (blue plot). Scan rate: 10 mV/s.